Mercury Concentrations in Fish: Implications of Dissolved Organic Matter (DOM) on Methylation Rates in Aquatic Systems

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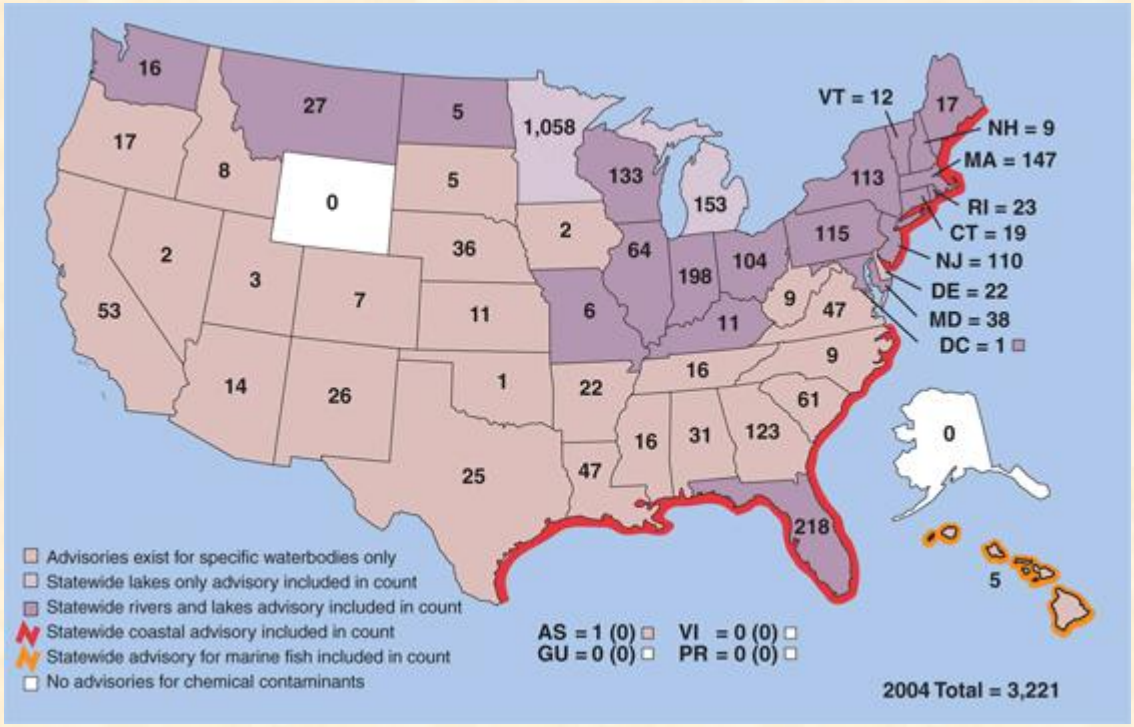
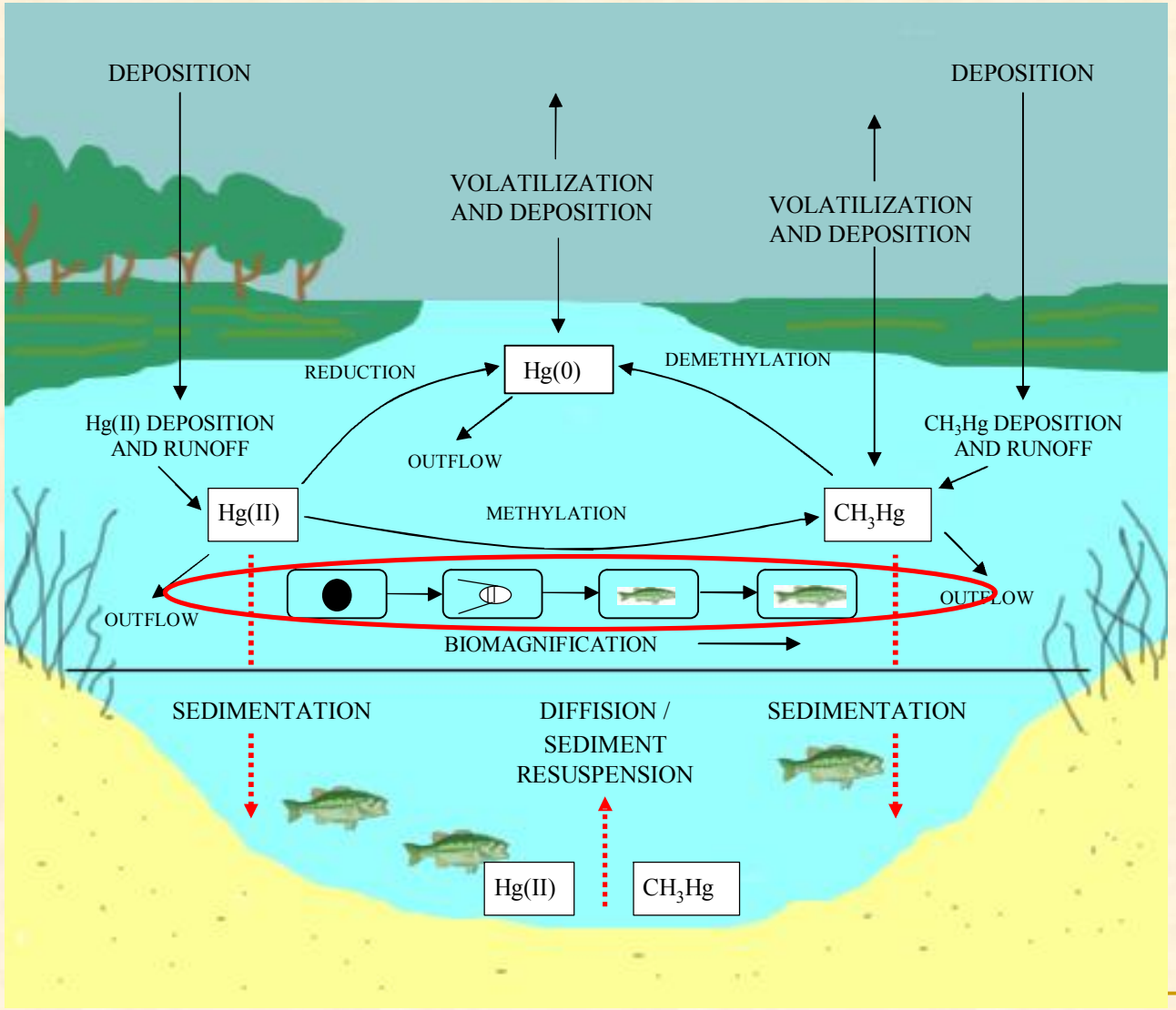
Just How Much Mercury is in the Environment?

- **High enough concentrations to warrant the establishment of national fish consumption advisories**
- **Utah**
  - 2004- 3
  - 2007- 8
- **Advisories numbers are misleading**
  - Only waters sampled



Biogeochemical Cycle of Mercury



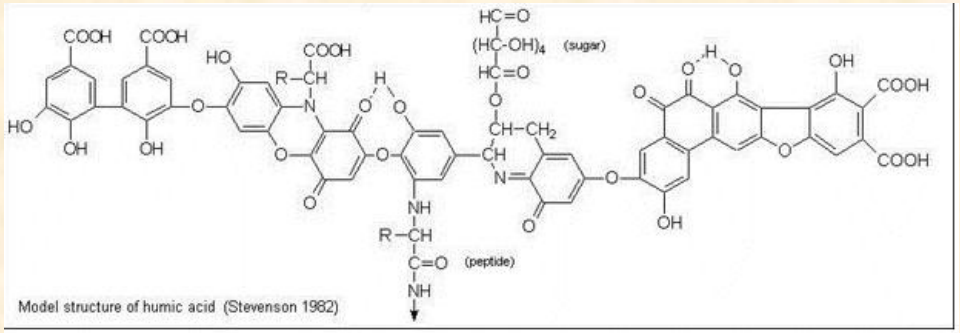
- Mercury participates in a large biogeochemical cycle
  - Air
  - Soil
  - Water
- Speciation important
  - Elemental
    - Hg^0
  - Inorganic
    - Hg(II)
  - Organic/Methyl
    - CH_3Hg
    - Can be methylated in water column or in aquatic organism

Environmental Ligands

- **Rarely does Hg exist as the free ion in solution**
  - Generally complexed to ligands
- **Ligands of importance**
  - Chloride
  - Sulfur
  - DOM
- **DOM has numerous functional moieties available for complexation to metals**
  - Carboxylic (-COOH)
  - Phenolic (-OH)
  - Ketones (-C=O)
  - Aldehydes (-CH)
    ||
    O
- **Hg primarily complexes to the reduced sulfur sites in DOM**
  - Reported constants = $10^{22\text{-}28}$
- **Secondarily complex to oxygen-containing functional groups**
  - Reported constants = 10^{10}

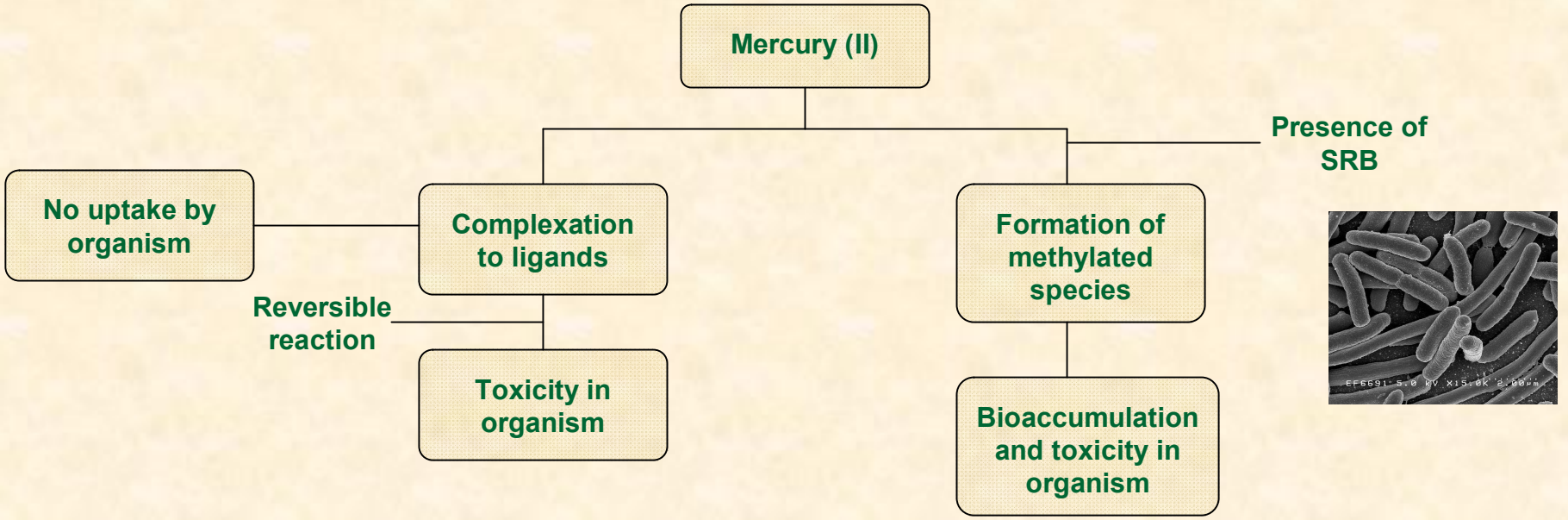
How Ligand Complexation Affects Metal Toxicity

- **A complexed metal is less bioavailable for uptake by organisms**
  - Cannot pass gills (fish), dermal layer (invertebrates)
  - Decreases toxicity
- **This trend has been documented in the literature for numerous metal-ligand combinations**
  - Cu
  - Ni
  - Zn
- **Little research on Hg complexation to ligands**
  - DOM is extremely complex, having numerous reactive functional moieties for metal binding



Mercury(II) vs. Methylmercury

- **Mercury(II) most prevalent form in natural waters; species required for methylation by sulfate-reducing bacteria (SRB)**
  - MeHg occurs when Hg(II) gains a methyl group ($-CH_3$)
- **Methylated species are ~ 100-1,000x more toxic to organisms than inorganic species**
- **Methylation by SRB only occurs in anoxic sediments; therefore, methylation follows temporal trends as well as deposition patterns**



Mercury Methylation

Factors Influencing Mercury Methylation Rates	
Physical or Chemical Condition	**Qualitative Influence on Methylation**
Low [DO]	Enhance methylation
Decrease pH	Enhance methylation
Increase [DOM]	Enhance methylation
Increase salinity	Inhibit methylation
Increase [nutrient]	Enhance methylation
Increase [selenium]	Inhibit methylation
Increase temperature	Enhance methylation
Increase [SO_4^{2-}]	Enhance methylation
Increase [S^{2-}]	Enhance methylation

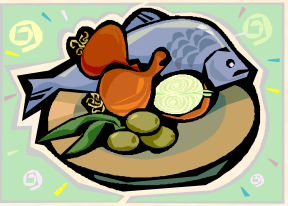
- **The potential for methylation is dependent on a variety of factors**
  - Favorable conditions: aquatic, acidic environments with high [DOM]
- **Enhancing methylation = higher MeHg = more bioaccumulation in fish**

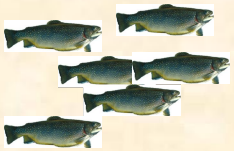
Methylation Potential

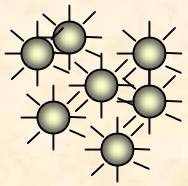
wetlands > lakes >>> rivers and streams

Mercury Bioaccumulation

- **Methylmercury accumulates through aquatic food webs**
  - Highest levels are in large predatory fish and fish-eating (piscivorous) animals
  - **Mercury levels in fish are 1-10 million fold higher than levels in water**
- **Extent of bioaccumulation is highly variable and hard to predict from one water body to another**
  - Food chain length
  - Number and type of organisms in food chain







Human consumption

Large predatory fish

Small forage fish

Zooplankton and Shellfish

Algae/ Phytoplankton

Bioaccumulation potential

Fundamental Questions: The Role of Mercury and DOM to Aquatic Toxicity

- What is the relationship between the amount of Hg in atmospheric deposition and the amount of methylmercury in fish?
- How quickly will the fish Hg levels respond to a change/reduction in mercury deposition?
- How will environmental factors affect the magnitude and timing of the response?

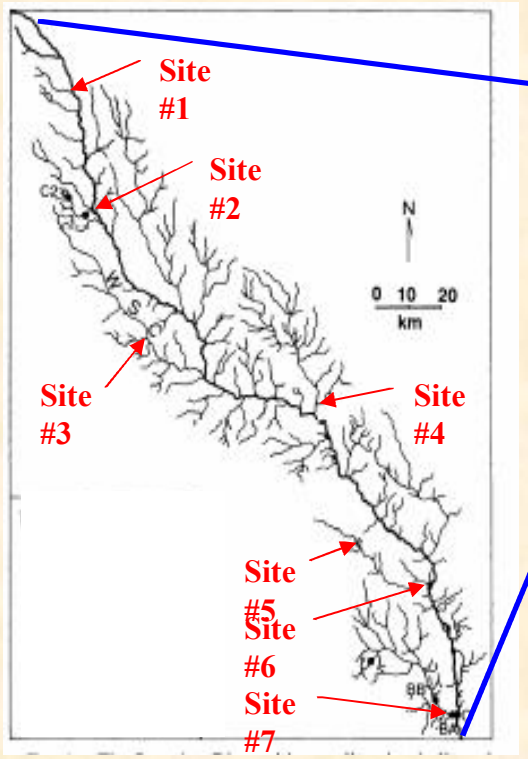
Aquatic and Terrestrial Fate of Mercury: Freshwaters

- **Some recent evidence of more rapid responses to reductions in mercury loadings**
  - METAALICUS:
    - Scientists added small amounts of isotopically labeled mercury to a lake ecosystem to trace its movement through the system
      - Mercury deposited to the lake surface was found in perch within a few months
      - After a year this mercury comprised 15% of the mercury found in 1 yr old perch
      - Results seem to indicate that older mercury is less available for methylation. This suggests that the lake would respond quickly to reduction in loading.
        - Role of DOM?
  - Florida Everglades:
    - Large reductions in loadings in the early 1990s due to bans on mercury in batteries and paints. Further reductions in late 1990s and early 2000s due to regulations requiring emissions reductions from municipal waste combustors
    - Levels in game fish have fallen 60-70 percent
    - Older, drier systems may respond more slowly

METAALICUS

Mercury-DOM Toxicity Experiments

- **Objective: To determine the influence of mercury(II)-DOM complexation on toxicity to an aquatic organism**
- **Ogeechee River**
  - High [DOM]
- **Series of experiments**
  - **Whole site water**
    - Used unamended site water
  - Size fractionated site water
    - Different fractions ability to complex mercury
  - pH adjusted site water
    - Importance of pH
      - Low pH- more protonation of organic matter
      - High pH- metal solid precipitate out of solution



Mercury(II)-DOM Toxicity Results

- **Toxicity is independent of [DOM]**
  - Similar toxicity exhibited through all 7 sites
    - Reduction in toxicity of ~ 3x
  - No increase in reduction of toxicity with increasing [DOM]
- **Different DOM sources also examined**
  - Suwannee River DOM isolate
    - Similar results to those previously observed

Site	[DOM] (mg/L)	Observed LC_{50} (ug Hg/L)	95% Confidence Interval
1	3.569	9.07	7.78-10.58
2	5.182	8.52	6.93-10.47
3	5.663	9.25	7.82-10.94
4	5.847	10.08	8.75-11.61
5	7.272	9.93	8.48-11.63
6	7.947	11.55	10.02-13.31
7	8.965	10.03	8.66-11.63

What makes the toxicity of mercury so different than other metals?

Aquatic and Terrestrial Fate of Mercury: Saltwaters

- **Less is known about the fate of mercury in saltwater environments and extent or speed with which it responds to a change in deposition**
- **Marine systems**
  - Large, fish-eating fish have been measured with very high levels of mercury (i.e., shark, swordfish)
  - Where the mercury in ocean fish comes from?
- **Estuarine and coastal systems**
  - High levels of mercury have been measured in some fish (i.e., king mackerel)
  - More data being developed on systems (i.e., Long Island Sound)
- **Because salt water fish is a major source of nutrition for many people around the world, this is a critical area of research**

Mercury and DOM: New Insights

- **"Waterborne Carbon Increases Threat of Environmental Mercury"- Presented at the American Geophysical Union meeting by John Moreau on 12/10/2007 (http://www.sciencedaily.com/releases/2007/12/071210162850.htm)**
  - Presence of DOM increases biological risk of aqueous mercury; may serve as an environmental source
  - In studies, higher and more efficient rates of methylation were observed in the presence of DOM
  - DOM from different sources have varying positive effects on methylation
  - Due to DOM's ubiquitous nature, its effect on the processing of mercury is an important factor in quantifying mercury bioavailability
  - Currently examining how DOM promotes methylation
    - DOM acts indirectly by increasing bacterial growth
      - More SRB = more methylation
      - DOM may interact with the mercury to boost its ability to enter bacteria

Mercury and DOM: Future Direction

- **Better understanding of biogeochemical cycle of mercury**
  - Why are specific waters susceptible to mercury contamination while others seem impervious?
- **Better define the relationship between mercury and DOM in aquatic systems**
  - How does DOM enhance/inhibit mercury methylation?
    - Better understanding of the methylation process
  - Why is mercury toxicity independent of [DOM]?
    - Chemical/physiochemical interactions